

# PATENT ABSTRACTS OF JAPAN

(11) Publication number : 2000-243463  
(43) Date of publication of application : 08. 09. 2000

---

(51) Int. Cl. H01M 14/00  
H01L 31/04

---

(21) Application number : 11-041299 (71) Applicant : FUJI XEROX CO LTD

(22) Date of filing : 19. 02. 1999 (72) Inventor : IMAI AKIRA  
SATO KATSUHIRO  
HIROSE HIDEKAZU  
TAKADA HOKUTO

---

(54) OPTICAL SEMICONDUCTOR ELECTRODEPHOTOELECTRIC CONVERTER AND  
PHOTOELECTRIC CONVERSION METHOD

(57) Abstract:

PROBLEM TO BE SOLVED: To efficiently utilize sunlight by providing a photoelectric conversion layer of one kind or more of a tetracyanoanthraquinodimethane compound and a perylene compound on the surface of a metal oxide semiconductor.

SOLUTION: This tetracyanoanthraquinodimethane compound is shown in a formula I. In the formula IR1 and R2 are a hydrogen atomalkyl grouparyl groupalkyl groupalkoxyalkyl group or acyl group; n is 0 or 1. This perylene compound is shown in a formula II. In the formula IIR3 and R4 are a group represented by a formula IIIetc.; when the R3 and R4 are a group represented by the formula III1 is 0. In the formula IIIR5 and R6 are an aliphatic grouparomatic group or heterocyclic group; these may be substituted by a substituent. A1 represents a bivalent aliphatic grouparomatic group or heterocyclic group; these may be substituted by a substituent.

---

CLAIMS

---

[Claim(s)]

[Claim 1] An optical semiconductor electrode having a photoelectric

conversion layer by at least one sort chosen from a perylene compound expressed with a tetracyano anthra quinodimethane compound and following general formula (II) which are expressed with following general formula (I) on the surface of a metal oxide semiconductor.

General formula (I)

[Formula 1]

In said general formula (I) $R^1$  and  $R^2$  It may be mutually the same and may differ a hydrogen atom an alkyl group an aryl group an aralkyl group an alkoxyalkyl group or an acyl group may be expressed and these may form the annular group of the following structure mutually. n expresses 0 or 1.

[Formula 2]

General formula (II)

[Formula 3]

In said general formula (II) $R^3$  and  $R^4$  Expressing the basis expressed with either following general formula (III) – (IX) these may be mutually the same it may differ and at least one side expresses the basis expressed with either following general formula (III) – (VII) and (IX). 1 expresses 0–12 when it is a basis which expresses 0 when  $R^3$  and  $R^4$  are the bases expressed with either following general formula (III) – (VIII) and is expressed with following general formula (IX).

General formula (III)

[Formula 4]

In said general formula (III) $R^5$  and  $R^6$  may be mutually the same it may differ an aliphatic group an aromatic group or a heterocycle group is expressed and these may be replaced by the substituent.  $A^1$  expresses a divalent aliphatic group an aromatic group or a heterocycle group and these may be replaced by the substituent.

General formula (IV)

[Formula 5]

In said general formula (IV) $A^2$  expresses a divalent aliphatic group an aromatic group or a heterocycle group and these may be replaced by the

substituent. R<sup>7</sup> and R<sup>8</sup> may be mutually the same and it may differ A hydrogen atom or a halogen atom or the alkyl group of the carbon numbers 1-20- (CH<sub>2</sub>)<sub>p</sub>COOR<sup>18</sup>- (CH<sub>2</sub>)<sub>p</sub>SO<sub>3</sub>R<sup>19</sup> or -(CH<sub>2</sub>)<sub>p</sub>NR<sup>20</sup>R<sup>21</sup> is expressed. R<sup>18</sup>R<sup>19</sup>R<sup>20</sup> and R<sup>21</sup> express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.

General formula (V)

[Formula 6]

In said general formula (V) A<sup>3</sup> expresses a single bond or a divalent aliphatic group or an aromatic group or a heterocycle group and these may be replaced by the substituent. R<sup>9</sup> expresses an aliphatic group or an aromatic group or a heterocycle group and these may be replaced by the substituent. R<sup>10</sup> A hydrogen atom or a halogen atom or the alkyl group of the carbon numbers 1-20- (CH<sub>2</sub>) Express (CH<sub>2</sub>)<sub>p</sub>COOR<sup>18</sup>- (CH<sub>2</sub>)<sub>p</sub>SO<sub>3</sub>R<sup>19</sup> or -(CH<sub>2</sub>)<sub>p</sub>NR<sup>20</sup>R<sup>21</sup>. R<sup>18</sup>R<sup>19</sup>R<sup>20</sup> and R<sup>21</sup> express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.

General formula (VI)

[Formula 7]

In said general formula (VI) A<sup>4</sup> expresses a divalent aliphatic group or an aromatic group or a heterocycle group and these may be replaced by the substituent. X expresses an oxygen atom or a sulfur atom or >NR<sup>22</sup>. R<sup>11</sup> and R<sup>12</sup> A hydrogen atom or a halogen atom or the alkyl group of the carbon numbers 1-20- (CH<sub>2</sub>) Express (CH<sub>2</sub>)<sub>p</sub>COOR<sup>18</sup>- (CH<sub>2</sub>)<sub>p</sub>SO<sub>3</sub>R<sup>19</sup> or -(CH<sub>2</sub>)<sub>p</sub>NR<sup>20</sup>R<sup>21</sup>. R<sup>18</sup>R<sup>19</sup>R<sup>20</sup>R<sup>21</sup> and R<sup>22</sup> express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.

General formula (VII)

[Formula 8]

In said general formula (VII) A<sup>5</sup> expresses a single bond or a divalent aliphatic group or an aromatic group or a heterocycle group and these may be replaced by the substituent. R<sup>13</sup> expresses a divalent aliphatic group or an aromatic group or a heterocycle group and these may be replaced by the substituent. R<sup>14</sup> A hydrogen atom or a halogen atom or the alkyl group of the carbon numbers 1-20- (CH<sub>2</sub>) Express (CH<sub>2</sub>)<sub>p</sub>COOR<sup>18</sup>- (CH<sub>2</sub>)<sub>p</sub>SO<sub>3</sub>R<sup>19</sup> or -(CH<sub>2</sub>)<sub>p</sub>NR<sup>20</sup>R<sup>21</sup>. R<sup>18</sup>R<sup>19</sup>R<sup>20</sup> and R<sup>21</sup> express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.

General formula (VIII)

[Formula 9]

In said general formula (VIII)A<sup>6</sup> expresses a divalent aliphatic group aromatic group or heterocycle group and these may be replaced by the substituent. Y expresses -COOH-SOOH or -NH<sub>2</sub>.

General formula (IX)

[Formula 10]

In said general formula (IX)X expresses two hydrogen atoms or MgZnFeConickelCuRuSnSnOTiOVAluminum (OH)Ga (OH) or In (OH). R<sup>15</sup>R<sup>16</sup> and R<sup>17</sup> express a hydrogen atom or halogen atom the alkyl group of the carbon numbers 1-12-(CH<sub>2</sub>)<sub>m</sub>COOH or -(CH<sub>2</sub>)<sub>m</sub>NH<sub>2</sub>. m and n express the integer of 0-12.

[Claim 2] The optical semiconductor electrode according to claim 1 whose tetracyano anthra quinodimethane compound expressed with said general formula (I) is a tetracyano anthra quinodimethane compound expressed with a following general formula (I-a).

A general formula (I-a)

[Formula 11]

In said general formula (I-a)Me expresses a methyl group. n expresses 0 or 1.

[Claim 3] The optical semiconductor electrode according to claim 1 or 2 whose metal oxide semiconductor is at least one sort chosen from titanium oxidetin oxidetungstic oxide a zinc oxide indium oxideniobium oxidenickel oxide cobalt oxide and strontium titanate.

[Claim 4] A photoelectric conversion device which has at least a connecting means which connects an electrode of a couple contacted to an electrolyte and an electrode of this couple so that energization is possible and is characterized by at least one side of an electrode of this couple being the optical semiconductor electrode according to any one of claims 1 to 3.

[Claim 5] It is the photoelectric conversion method of contacting an electrode of a couple mutually connected so that energization was possible to an electrolyte and producing a photoelectric conversion reaction by irradiating at least one side of an electrode of this couple. A photoelectric conversion method that an electrode with which light is irradiated is characterized by being the optical semiconductor

electrode according to any one of claims 1 to 3.

---

## DETAILED DESCRIPTION

---

### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to the optical semiconductor electrode to which the specific compound was made to stick on the surface of a metal oxide semiconductor the photoelectric conversion device using it and the photoelectric conversion method.

#### [0002]

[Description of the Prior Art] In recent years use of sunlight attracts attention as an energy resource replaced with fossil fuelssuch as petroleum and coal. As a device which transforms light energy into electrical energy directlythe dry type solar cell in which pn junction was formed on inorganic semiconductorssuch as silicon and gallium arsenideis known welland it is put in practical use as a power supply of the object for remote placesor a portable electronic deviceetc. Howeverconversion efficiency with these expensive solar cells is acquired.

On the other handsince the energy and cost which manufacture takes are very highthere is a problem that it is difficult to use as an energy resource.

[0003]The wet solar cell whichon the other handused the photoelectrochemical reaction which occurs by the interface of a semiconductor and an electrolytic solution as an option which transforms light energy into electrical energy is known. As compared with the above-mentioned silicongallium arsenideetc. metal oxide semiconductors used heresuch as titanium oxidetin oxideand a zinc oxidecan be manufactured at far low energy and costand are expected as a future energy conversion material. Howeversince a stable metal oxide semiconductor like titanium oxide has the band gap as large as not less than 3 eVonly about 4% of ultraviolet radiation of sunlight can be usedandthe way things standhigh conversion efficiency cannot be expected. On the surface of these metal oxide semiconductorsas sensitizing dye Thencyanine dye and a xanthene dyeorganic coloring matter (H. -- Tsubomura et. al. Nature. 261and 402 (1976).)such as coumarin coloring matter M. To make Matsumura et. al. Bull. Chem. Soc. Jpn. 502533 (1977) JP10-92477AJP10-93118Aetc. adsorb and to carry out spectral sensitization is

tried. However when the above-mentioned cyanine dyea xanthene dyecoumarin coloring matteretc. are used there is a problem that photoelectric conversion efficiency is not enough.

[0004]

[Problem(s) to be Solved by the Invention] This invention solves many problems in said former and makes it a technical problem to attain the following purposes. That is this invention can carry out available [ of the sunlight ] efficiently and is excellent in photoelectric conversion efficiency stability endurance etc. and an object of this invention is to provide the photoelectric conversion device and the photoelectric conversion method of excelling in photoelectric conversion efficiency using the optical semiconductor electrode which can be manufactured cheaply and easily and this optical semiconductor electrode.

[0005]

[Means for Solving the Problem] Said The means for solving a technical problem is as follows. That is it is an optical semiconductor electrode having a photoelectric conversion layer by at least one sort chosen as the surface of <1> metal oxide semiconductor from a perylene compound expressed with a tetracyano anthra quinodimethane compound and following general formula (II) which are expressed with following general formula (I).

General formula (I)

[0006]

[Formula 12]

[0007] In said general formula (I) R<sup>1</sup> and R<sup>2</sup> It may be mutually the same and may differ a hydrogen atom an alkyl group an aryl group an aralkyl group an alkoxyalkyl group or an acyl group may be expressed and these may form the annular group of the following structure mutually. n expresses 0 or 1.

[0008]

[Formula 13]

[0009] General formula (II)

[Formula 14]

[0010] In said general formula (II) R<sup>3</sup> and R<sup>4</sup> Expressing the basis expressed with either following general formula (III) - (IX) these may be mutually the same it may differ and at least one side expresses the basis

expressed with either following general formula (III) - (VII) and (IX).  
1 expresses 0-12 when it is a basis which expresses 0 when R<sup>3</sup> and R<sup>4</sup> are  
the bases expressed with either following general formula (III) -  
(VIII) and is expressed with following general formula (IX).

General formula (III)

[0011]

[Formula 15]

[0012] In said general formula (III) R<sup>5</sup> and R<sup>6</sup> may be mutually the same it  
may differ an aliphatic group an aromatic group or a heterocycle group is  
expressed and these may be replaced by the substituent. A<sup>1</sup> expresses a  
divalent aliphatic group an aromatic group or a heterocycle group and these may  
be replaced by the substituent.

General formula (IV)

[0013]

[Formula 16]

[0014] In said general formula (IV) A<sup>2</sup> expresses a divalent aliphatic  
group an aromatic group or a heterocycle group and these may be replaced by the  
substituent. R<sup>7</sup> and R<sup>8</sup> may be mutually the same and it may differ.  
A hydrogen atom a halogen atom the alkyl group of the carbon numbers 1-20-  
 $(CH_2)_pCOOR^{18}-(CH_2)_pSO_3R^{19}$  or  $-(CH_2)_pR^{20}R^{21}$  is expressed. R<sup>18</sup>R<sup>19</sup>R<sup>20</sup> and R<sup>21</sup>  
express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p  
expresses the integer of 0-20.

General formula (V)

[0015]

[Formula 17]

[0016] In said general formula (V) A<sup>3</sup> expresses a single bond or a  
divalent aliphatic group an aromatic group or a heterocycle group and these  
may be replaced by the substituent. R<sup>9</sup> expresses an aliphatic group an  
aromatic group or a heterocycle group and these may be replaced by the  
substituent. R<sup>10</sup> A hydrogen atom a halogen atom the alkyl group of the  
carbon numbers 1-20- Express  $pCOOR^{18}-(CH_2)_pSO_3R^{19}$  or  $-(CH_2)_pNR^{20}R^{21}$ .  
R<sup>18</sup>R<sup>19</sup>R<sup>20</sup> and R<sup>21</sup> express the alkyl group of a hydrogen atom or the carbon  
numbers 1-20. p expresses the integer of 0-20.

General formula (VI)

[0017]

[Formula 18]

[0018] In said general formula (VI) A<sup>4</sup> expresses a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by a substituent. X expresses an oxygen atom or sulfur atom or >NR<sup>22</sup>. R<sup>11</sup> and R<sup>12</sup> A hydrogen atom or halogen atom or alkyl group of the carbon numbers 1-20- (CH<sub>2</sub>) Express <sub>p</sub>COOR<sup>18</sup>- (CH<sub>2</sub>) <sub>p</sub>SO<sub>3</sub>R<sup>19</sup> or -(CH<sub>2</sub>) <sub>p</sub>NR<sup>20</sup>R<sup>21</sup>. R<sup>18</sup>R<sup>19</sup>R<sup>20</sup>R<sup>21</sup> and R<sup>22</sup> express an alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses an integer of 0-20.

General formula (VII)

[0019]

[Formula 19]

[0020] In said general formula (VII) A<sup>5</sup> expresses a single bond or a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by a substituent. R<sup>13</sup> expresses a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by a substituent. R<sup>14</sup> A hydrogen atom or halogen atom or alkyl group of the carbon numbers 1-20- (CH<sub>2</sub>) Express <sub>p</sub>COOR<sup>18</sup>- (CH<sub>2</sub>) <sub>p</sub>SO<sub>3</sub>R<sup>19</sup> or -(CH<sub>2</sub>) <sub>p</sub>NR<sup>20</sup>R<sup>21</sup>. R<sup>18</sup>R<sup>19</sup>R<sup>20</sup> and R<sup>21</sup> express an alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses an integer of 0-20.

General formula (VIII)

[0021]

[Formula 20]

[0022] In said general formula (VIII) A<sup>6</sup> expresses a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by a substituent. Y expresses -COOH-SOOH or -NH<sub>2</sub>.

General formula (IX)

[0023]

[Formula 21]

[0024] In said general formula (IX) X expresses two hydrogen atoms or MgZnFeConickelCuRuSnSnOTiOVOaluminum (OH)Ga (OH) or In (OH). R<sup>15</sup>R<sup>16</sup> and R<sup>17</sup> express a hydrogen atom or halogen atom or the alkyl group of the carbon numbers 1-12- (CH<sub>2</sub>) <sub>m</sub>COOH or -(CH<sub>2</sub>) <sub>m</sub>NH<sub>2</sub>. m and n express the integer of 0-12.

<2> A tetracyano anthra quinodimethane compound expressed with said general formula (I) is an optical semiconductor electrode given in the above <1> which is a tetracyano anthra quinodimethane compound expressed with a following general formula (I-a).

General formula (I-a)

[0025]

[Formula 22]

[0026] In said general formula (I-a) $M_e$  expresses a methyl group.  $n$  expresses 0 or 1.

<3> metal oxide semiconductors are optical semiconductor electrodes given in the above <1> or <2> which is at least one sort chosen from titanium oxide the tin oxidetungstic oxide a zinc oxide indium oxide niobium oxide nickel oxide cobalt oxide and strontium titanate.

It has at least a connecting means which connects the electrode of the couple contacted to <4> electrolytes and the electrode of this couple so that energization is possible and at least one side of the electrode of this couple is a photoelectric conversion device characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <3>.

<5> An electrode of a couple mutually connected so that energization was possible is contacted to an electrolyte. By irradiating at least one side of an electrode of this couple it is the photoelectric conversion method of producing a photoelectric conversion reaction and an electrode with which light is irradiated is the photoelectric conversion method characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <3>.

[0027]

[Embodiment of the Invention] (Optical semiconductor electrode) The optical semiconductor electrode of this invention has a photoelectric conversion layer by at least one sort chosen from the perylene compound expressed with the tetracyano anthra quinodimethane compound and following general formula (II) which are expressed with following general formula (I) on the surface of a metal oxide semiconductor.

[0028]- metal oxide semiconductor - As said metal oxide semiconductor there is no restriction in particular and it can choose suitably according to the purpose for example titanium oxide tin oxide tungstic oxide a zinc oxide indium oxide niobium oxide etc. are mentioned. These may be used by an one-sort independent and may use two or more sorts together. Especially in this invention the

reasons of a photoelectric transfer characteristicchemical stabilitymanufacture easeetc. to titanium oxide is preferred also in these.

[0029]About the shape of said metal oxide semiconductor structureand a sizethere is no restriction in particular and it can choose suitably according to the purpose. For exampleas a structure of said metal oxide semiconductorIt may be the structure which consists only of this metal oxide semiconductorand may be the structure in which the thin film layer of this metal oxide semiconductor was formed on conductive base materialssuch as platenesssuch as transparent electrodessuch as ITO glass and Nesa glassplatinumcopperand black leador a mesh electrode.

[0030]- photoelectric conversion layer - The surface of said metal oxide semiconductor is adsorbed in at least one sort chosen from the perylene compound expressed with the tetracyano anthra quinodimethane compound and following general formula (II) which are expressed with following general formula (I)and said photoelectric conversion layer is formed in it.

General formula (I)

[0031]

[Formula 23]

[0032]In said general formula (I) $R^1$  and  $R^2$ It may be mutually the sameand may differa hydrogen atoman alkyl groupan aryl groupan aralkyl groupan alkoxyalkyl groupor an acyl group may be expressedand these may form the annular group of the following structure mutually. n expresses 0 or 1.

[0033]

[Formula 24]

General formula (II)

[Formula 25]

[0034]In said general formula (II) $R^3$  and  $R^4$ Expressing the basis expressed with either following general formula (III) - (IX)these may be mutually the sameit may differ and at least one side expresses the basis expressed with either following general formula (III) - (VII) and (IX). 1 expresses 0when it is a basis which expresses 0 when  $R^3$  and  $R^4$  are the bases expressed with either following general formula (III) - (VIII)and is expressed with following general formula (IX).

General formula (III)

[0035]

[Formula 26]

[0036] In said general formula (III) R<sup>5</sup> and R<sup>6</sup> may be mutually the same it may differ an aliphatic group an aromatic group or a heterocycle group is expressed and these may be replaced by a substituent. A<sup>1</sup> expresses a divalent aliphatic group an aromatic group or a heterocycle group and these may be replaced by a substituent.

General formula (IV)

[0037]

[Formula 27]

[0038] In said general formula (IV) A<sup>2</sup> expresses a divalent aliphatic group an aromatic group or a heterocycle group and these may be replaced by the substituent. R<sup>7</sup> and R<sup>8</sup> may be mutually the same and it may differ. A hydrogen atom or a halogen atom the alkyl group of the carbon numbers 1-20- (CH<sub>2</sub>)<sub>p</sub>COOR<sup>18</sup>- (CH<sub>2</sub>)<sub>p</sub>SO<sub>3</sub>R<sup>19</sup> or - (CH<sub>2</sub>)<sub>p</sub>NR<sup>20</sup>R<sup>21</sup> is expressed. R<sup>18</sup>R<sup>19</sup>R<sup>20</sup> and R<sup>21</sup> express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.

General formula (V)

[0039]

[Formula 28]

[0040] In said general formula (V) A<sup>3</sup> expresses a single bond or a divalent aliphatic group an aromatic group or a heterocycle group and these may be replaced by the substituent. R<sup>9</sup> expresses an aliphatic group an aromatic group or a heterocycle group and these may be replaced by the substituent. R<sup>10</sup> A hydrogen atom or a halogen atom the alkyl group of the carbon numbers 1-20- (CH<sub>2</sub>) Express pCOOR<sup>18</sup>- (CH<sub>2</sub>)<sub>p</sub>SO<sub>3</sub>R<sup>19</sup> or - (CH<sub>2</sub>)<sub>p</sub>NR<sup>20</sup>R<sup>21</sup>. R<sup>18</sup>R<sup>19</sup>R<sup>20</sup> and R<sup>21</sup> express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.

General formula (VI)

[0041]

[Formula 29]

[0042] In said general formula (VI) A<sup>4</sup> expresses a divalent aliphatic

grouparomatic groupor heterocycle groupand these may be replaced by the substituent. X expresses an oxygen atom or sulfur atom or  $>NR^{22}$ . R<sup>11</sup> and R<sup>12</sup> A hydrogen atom or halogen atomthe alkyl group of the carbon numbers 1-20- (CH<sub>2</sub>) Express <sub>p</sub>COOR<sup>18</sup>- (CH<sub>2</sub>) <sub>p</sub>SO<sub>3</sub>R<sup>19</sup>or -(CH<sub>2</sub>) <sub>p</sub>NR<sup>20</sup>R<sup>21</sup>. R<sup>18</sup>R<sup>19</sup>R<sup>20</sup>R<sup>21</sup>and R<sup>22</sup> express the alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses the integer of 0-20.

General formula (VII)

[0043]

[Formula 30]

[0044]In said general formula (VII)A<sup>5</sup> expresses a single bond or a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by a substituent. R<sup>13</sup> expresses a divalent aliphatic groupan aromatic groupor a heterocycle groupand these may be replaced by a substituent. R<sup>14</sup> A hydrogen atom or halogen atom an alkyl group of the carbon numbers 1-20- (CH<sub>2</sub>) Express <sub>p</sub>COOR<sup>18</sup>- (CH<sub>2</sub>) <sub>p</sub>SO<sub>3</sub>R<sup>19</sup>or -(CH<sub>2</sub>) <sub>p</sub>NR<sup>20</sup>R<sup>21</sup>. R<sup>18</sup>R<sup>19</sup>R<sup>20</sup>and R<sup>21</sup> express an alkyl group of a hydrogen atom or the carbon numbers 1-20. p expresses an integer of 0-20.

General formula (VIII)

[0045]

[Formula 31]

[0046]In said general formula (VIII)A<sup>6</sup> expresses a divalent aliphatic grouparomatic groupor heterocycle groupand these may be replaced by the substituent. Y expresses -COOH-SOOH or -NH<sub>2</sub>.

General formula (IX)

[0047]

[Formula 32]

[0048]In said general formula (IX)X expresses two hydrogen atoms or MgZnFeConickelCuRuSnSnOTiOV0aluminum (OH)Ga (OH) or In (OH). R<sup>15</sup>R<sup>16</sup>and R<sup>17</sup> express a hydrogen atom or halogen atomthe alkyl group of the carbon numbers 1-12- (CH<sub>2</sub>) <sub>m</sub>COOH or -(CH<sub>2</sub>) <sub>m</sub>NH<sub>2</sub>. m and n express the integer of 0-12.

[0049]As a desirable example of a tetracyano anthra quinodimethane compound expressed with said general formula (I) the following compound (I-1-30) is mentioned. The example in n= 0 was shown in Table 1 and the example in n= 1 was shown in Table 2.

[0050]  
[Table 1]

[0051]  
[Table 2]

[0052] In this invention especially a tetracyano anthra quinodimethane compound that are pointssuch as photoelectric conversion efficiencyan absorption wavelength regionand an ease of manufactureand is expressed with a following general formula (I-a) also in these is preferred (compound expressed with said illustration compound (I-1)).

General formula (I-a)

[0053]  
[Formula 33]

In said general formula (I-a)Me expresses a methyl group. n expresses 0 or 1.

[0054] A tetracyano anthra quinodimethane compound expressed with said general formula (I)For exampleit is compoundable by method to which the Anthraquinone derivative expressed with a following general formula (A) of a statement to JP63-104062A and malononitrile expressed with a following general formula (B) are made to reactor a method given in JP58-55450A etc.

[0055]  
[Formula 34]

[0056]  
[Formula 35]

[0057] Efficientlyseparation and since it is movablethe tetracyano anthra quinodimethane compound expressed with said general formula (I) is efficientand can carry out spectral sensitization of the electric charge which it had an electronic receptiveness portion and an electron-donative portionand the absorption wavelength region is extended to the long wavelength region which is about 700 nm and was generated.

[0058] The following compound (II-1 ~ 13) is mentioned as a desirable

example of a perylene compound expressed with said general formula (II).

[0059]

[Formula 36]

[0060]

[Formula 37]

[0061]

[Formula 38]

[0062]

[Formula 39]

[0063]

[Formula 40]

[0064]

[Formula 41]

[0065]

[Formula 42]

[0066]

[Formula 43]

[0067]

[Formula 44]

[0068]

[Formula 45]

[0069]  
[Formula 46]

[0070]  
[Formula 47]

[0071]  
[Formula 48]

[0072] In this invention a following general formula (IX-a) is held as a perylene compound expressed with said general formula (II).

General formula (IX-a)

[0073]  
[Formula 49]

[0074] As a desirable example of a perylene compound expressed with said general formula (IX-a) the compound (IX-1 - 23) shown in Table 3 is mentioned.

[0075]  
[Table 3]

In Table 3 H<sub>2</sub> expresses two hydrogen atoms.

[0076] In the perylene compound which is said general formula (II) and is expressed R<sup>3</sup> and R<sup>4</sup> are the same what is a basis expressed with either said general formula (III) - (IX) respectively is compoundable by for example making a 3,4,9,10-perylene tetracarboxylic anhydride and the compound expressed with following general formula (III') - (IX') respectively react.

[0077]  
[Formula 50]

[0078]  
[Formula 51]

[0079]  
[Formula 52]

[0080]  
[Formula 53]

[0081]  
[Formula 54]

[0082]  
[Formula 55]

[0083]  
[Formula 56]

[0084] In a perylene compound which is said general formula (II) and is expressed R<sup>3</sup> differs from R<sup>4</sup> mutually. What is a basis expressed with either said general formula (III) - (IX). For example by making two sorts chosen from a 34910-perylene tetracarboxylic anhydride and a compound expressed with said general formula (III') - (IX') react or it is compoundable by making two sorts chosen from a compound expressed with 34910-perylene tetracarboxylic monoanhydride mono- metal salt and said general formula (III') - (IX') of a statement by United States patent 4<sup>th</sup> the No. 501 or 906 specification etc. react one by one.

[0085] A perylene compound expressed with said general formula (II) is excellent in chemical stability and endurance and is excellent in holdout in the surface of said metal oxide semiconductor and spectral sensitization can be carried out stably and efficient over a long period of time.

[0086] Formation of - photoelectric conversion layer - Said photoelectric conversion layer adds to a solvent at least one sort chosen from a perylene compound expressed with a tetracyano anthra quinodimethane compound expressed with said general formula (I) and said (II). It can form in the surface of this metal oxide semiconductor easily by immersing said metal oxide semiconductor into a solution which dissolved this.

[0087] As said solvent profitably there is no restriction and it can choose

from publicly known solvents suitably according to the purposeFor example amide system solventssuch as ketone solvents such as alcoholic solvents such as methanol and isopropyl alcohol acetone and methyl ethyl ketone N. N-dimethylformamide and N-methyl pyrrolidone water or these mixed solvents are mentioned. These may be used by an one-sort independent and may use two or more sorts together. Also in these amide system solventssuch as N. N-dimethylformamide are preferred. In this invention it is the purpose of raising solubility to said at least one sort chosen from a perylene compound expressed with a tetracyano anthra quinodimethane compound expressed with said general formula (I) and said (II) of solvents and acid an alkali etc. may be added in this solvent.

[0088] In order to promote adsorption to said at least one sort chosen from a perylene compound expressed with a tetracyano anthra quinodimethane compound which may perform said immersion at a room temperature and is expressed with said general formula (I) and said (II) of metal oxide semiconductors it may heat if needed.

[0089] After washing after said immersion using arbitrary solvents etc. by carrying out desiccation etc. An optical semiconductor electrode which has the photoelectric conversion layer by which at least one sort chosen from a perylene compound expressed with a tetracyano anthra quinodimethane compound expressed with said general formula (I) and said (II) was adsorbed and formed in the surface of said metal oxide semiconductor is obtained.

[0090] In a wide range of fields a semiconductor electrode of this invention can be used conveniently and can be used especially conveniently for the following photoelectric conversion devices and photoelectric conversion methods of this invention.

[0091] (Photoelectric conversion device) A photoelectric conversion device of this invention may have at least a connecting means which connects an electrode of a couple contacted to an electrolyte and an electrode of this couple so that energization is possible and also may have a means of others suitably selected if needed.

[0092] Also in an electrode of said couple it is an optical semiconductor electrode of said this invention and another side is a counterelectrode. As said counterelectrode to oxidation and reduction if stable there will be no restriction in particular and according to the purpose it can choose from a publicly known thing suitably for example transparent electrodes such as plate such as platinum gold and black lead ITO glass and Nesa glass etc. are mentioned.

[0093] A wire roda plate a printed film or a vacuum evaporation film etc. which restriction in particular does not have as long as it has a

function in which an electrode of said couple can be connected as said connecting means so that energization is possible and consists of conductive materialssuch as a publicly known lead or various metalcarbon and a metallic oxideis mentioned. This connecting means is connected to an electrode of said couple so that energization is possible.

[0094]As said electrolytethere is no restriction in particular and it can choose suitably according to the purposeFor examplesaltssuch as potassium chloridea lithium chlorideand tetraethylammonium perchlorateNonaqueous solvent solutionssuch as acidssuch as alkalisuch as sodium hydroxide and potassium carbonatesulfuric acidand chloridethese mixturesthese solution or these alcoholand propylene carbonateetc. are mentioned. In this inventionit is the purposessuch as attaining stabilization of the photoelectric current characteristicand a redox reagent which produces an oxidation-reduction reaction still more nearly reversibly [such as potassium iodide iodineand p-benzoquinone] in said electrolyte may be added. A photoelectric conversion device of this invention can be used conveniently for a photoelectric conversion method of the following this inventions.

[0095] (A photoelectric conversion method) In a photoelectric conversion method of this inventionan electrode of said couple mutually connected so that energization was possible is contacted to said electrolyteand a photoelectric conversion reaction is produced by irradiating at least one side of an electrode of this couple. [0096]In an electrode of said couplean electrode with which light is irradiated is an optical semiconductor electrode of said this inventionand another side is said counterelectrode.

[0097]- In a photoelectric conversion device and a photoelectric conversion method of photoelectric conversion reaction-this inventiona photoelectric conversion reaction arises as follows. That issaid optical semiconductor electrode and said counterelectrode are first immersed into said electrolyte (solution). Nextmonochromatic light of at least one sort of absorption wavelength regions chosen as said optical semiconductor electrode from a perylene compound expressed with a tetracyano anthra quinodimethane compound expressed with said general formula (I)and said general formula (II)Or an exposure of white light or multicolor light which includes one of the zones will transform such light energies into electrical energy.

[0098]According to a photoelectric conversion device and a photoelectric conversion method using a semiconductor electrode and this semiconductor electrode of this invention. Even if it irradiates with 300-700-nm

visible light as a light with which it irradiates especially good photoelectric conversion efficiency is acquired metal oxide semiconductor such as titanium oxide -- if independent it can use effectively to a wavelength band of visible light which cannot be used and luminous energies such as sunlight can be efficiently transformed into electrical energy.

[0099]

[Example] Hereafter although the example of this invention is described this invention is not limited to these examples at all.

[0100] (Example 1) 25 ml of alt. titanic acid tetraisopropyl was added gradually agitating violently in the mixed solution of 150 ml of pure water and the concentrated nitric acid 1.54g (specific gravity: 1.38). Temperature up was carried out to 80 \*\* continuing churning furthermore churning was continued at the temperature for 8 hours and the milky stable titanium oxide colloidal solution was prepared. This titanium oxide colloidal solution was condensed to 40 ml at 30 \*\* under decompression of 30mmHg. Said titanium oxide colloidal solution was coated with the spin coat method on the glass substrate (the following "ITO glass substrate" is called) with which the layer of ITO was covered and was calcinated at 500 \*\* for 1 hour. This operation was repeated 3 times and the titanium oxide layer about 1.0 micrometer thick was formed on the ITO glass substrate. When the crystal structure of the obtained titanium oxide membrane was checked with the X-ray diffraction method it was a mixture of an anatase and a rutile type. The ITO glass substrate which supported said titanium oxide layer was used as a metal oxide semiconductor.

[0101] After making the solution which dissolved in 50 ml of N,N-dimethylformamide immerse 100 mg of said illustration compound (I-1) at about 90 \*\* for 12 hours this metal oxide semiconductor was washed in order of acetone and methanol and natural seasoning was carried out. By the above adsorption formation of the photoelectric conversion layer with said illustration compound (I-1) was carried out on the surface of said metallic-oxide N semiconductor.

[0102] Next the lead was connected to the layer portion of ITO covered by the glass substrate. The terminal area of said lead covered and adhered with the epoxy resin. The optical semiconductor electrode was produced by the above.

[0103] Drawing 1 is an approximate account figure for explaining the produced optical semiconductor electrode. The optical semiconductor electrode 1 has the layer 3 of ITO the titanium oxide layer 4 and the photoelectric conversion layer 5 with said illustration compound (I-1)

on the glass base material 2 at this order. The terminal area of the layer 3 of ITO and the lead 7 was covered with the epoxy resin as the adhesive agent 6 and has adhered with it.

In this terminal area the lead 7 is accommodated into the glass tube 8.

[0104] Drawing 2 is an approximate account figure for explaining the photoelectric conversion method using the photoelectric conversion device provided with said optical semiconductor electrode. Here saturated calomel electrode \*\* is immersed in a platinum electrode as the optical semiconductor electrode 1 and the counterelectrode 9 which were produced and is immersed into the inside of the transparent glass cell 13 and the electrolytic solution 11 as the reference electrode 10. The electrolytic solutions 11 are 0.1M-sodium sulfate / 0.02M-potassium iodide solution. It is connected to the potentiostat 12 via the lead 7 as a connecting means and energization of each electrode is attained.

[0105] In this photoelectric conversion device it held so that the potential of said optical semiconductor electrode 1 might be set to 0V to the reference electrode 10 and it irradiated with white light (the xenon lamp of 500W illumination 4000lux) from the back side of the optical semiconductor electrode and the value of the photoelectric current at this time was measured with the potentiostat. The measurement result was shown in Table 4.

[0106] (Example 2) In Example 1 the outside which replaced the illustration compound (I-1) with the illustration compound (I-3) produced the optical semiconductor electrode and the photoelectric conversion device like Example 1 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 4.

[0107] (Example 3) In Example 1 the outside which replaced the illustration compound (I-1) with the illustration compound (I-7) produced the optical semiconductor electrode and the photoelectric conversion device like Example 1 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 4.

[0108] (Comparative example 1) In Example 1 the outside which did not use an illustration compound (I-1) produced the optical semiconductor electrode and the photoelectric conversion device like Example 1 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 4.

[0109] (Comparative example 2) The outside which replaced the illustration compound (I-1) with 2457-tetraiodofluorescein in Example 1

is an example. The optical semiconductor electrode and the photoelectric conversion device were produced like 1the photoelectric conversion method was enforcedand photoelectric current was measured. The measurement result was shown in Table 4.

[0110] (Comparative example 3) The outside which replaced the illustration compound (I-1) with copper (tetra KARUBOKI phthalocyaninato) (II) in Example 1 is an example. The optical semiconductor electrode and the photoelectric conversion device were produced like 1the photoelectric conversion method was enforcedand photoelectric current was measured. The measurement result was shown in Table 4.

[0111]

[Table 4]

[0112] (Example 4) In Example 1a metal oxide semiconductor instead of making the solution which dissolved in 50 ml of N,N-dimethylformamide immerse 100 mg of said illustration compound (I-1) at about 90 \*\* for 12 hoursThe outside in which the solution which dissolved in 50 ml of 2% hydroxylation tetra (n-butyl) ammonium / ethanol solutions was made to immerse 50 mg of an illustration compound (II-4) at 70-80 \*\* for 1 hour produces an optical semiconductor electrode and a photoelectric conversion device like Example 1and the photoelectric conversion method is enforcedPhotoelectric current was measured. The measurement result was shown in Table 5.

[0113] (Example 5) In Example 4the outside which replaced the illustration compound (II-4) with the illustration compound (II-9) produced the optical semiconductor electrode and the photoelectric conversion device like Example 4enforced the photoelectric conversion methodand measured photoelectric current. The measurement result was shown in Table 5.

[0114] (Example 6) In Example 4the outside which replaced the illustration compound (II-4) with the illustration compound (II-10) produced the optical semiconductor electrode and the photoelectric conversion device like Example 4enforced the photoelectric conversion methodand measured photoelectric current. The measurement result was shown in Table 5.

[0115] (Comparative example 4) In Example 4the outside which did not use an illustration compound (II-4) produced the optical semiconductor electrode and the photoelectric conversion device like Example 4enforced the photoelectric conversion methodand measured photoelectric current.

The measurement result was shown in Table 5.

[0116] (Comparative example 5) In Example 4 the outside which replaced the illustration compound (II-4) with 2457-tetraiodofluorescein produced the optical semiconductor electrode and the photoelectric conversion device like Example 4 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 5.

[0117]

[Table 5]

[0118] (Example 7) In Example 1 a metal oxide semiconductor instead of making the solution which dissolved in 50 ml of N,N-dimethylformamide immerse 100 mg of said illustration compound (I-1) at about 90 \*\* for 12 hours. The outside in which the solution which dissolved in 50 ml of N,N-dimethylformamide was made to immerse 100 mg of an illustration compound (IX-4) at 80-100 \*\* for 1 hour produced the optical semiconductor electrode and the photoelectric conversion device like Example 1 enforced the photoelectric conversion method and measured photoelectric current.

The measurement result was shown in Table 6.

[0119] (Example 8) In Example 7 the outside which replaced the illustration compound (IX-4) with the illustration compound (IX-7) produced the optical semiconductor electrode and the photoelectric conversion device like Example 7 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 6.

[0120] (Example 9) In Example 7 the outside which replaced the illustration compound (IX-4) with the illustration compound (IX-9) produced the optical semiconductor electrode and the photoelectric conversion device like Example 7 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 6.

[0121] (Comparative example 6) In Example 7 the outside which did not use an illustration compound (IX-4) produced the optical semiconductor electrode and the photoelectric conversion device like Example 7 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 6.

[0122] (Comparative example 7) In Example 7 the outside which replaced the illustration compound (IX-4) with 2457-tetraido-3'4'5'6'-tetrachlorofluorescein produced the optical semiconductor electrode and the photoelectric conversion device were produced like Example 7 the photoelectric conversion method was enforced and photoelectric current

was measured. The measurement result was shown in Table 6.

[0123] (Comparative example 8) In Example 7 the outside which replaced the illustration compound (IX-4) with copper (tetracarboxy phthalocyaninato) (II) produced the optical semiconductor electrode and the photoelectric conversion device like Example 7 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 6.

[0124]

[Table 6]

[0125]

[Effect of the Invention] According to this invention available [of the sunlight] can be carried out efficiently it excels in photoelectric conversion efficiency stability endurance etc. and the photoelectric conversion device and the photoelectric conversion method of excelling in photoelectric conversion efficiency can be provided using the optical semiconductor electrode which can be manufactured cheaply and easily and this optical semiconductor electrode.

---

#### DESCRIPTION OF DRAWINGS

---

[Brief Description of the Drawings]

[Drawing 1] Drawing 1 is an approximate account figure of the optical semiconductor electrode of this invention.

[Drawing 2] Drawing 2 is an approximate account figure for explaining the photoelectric conversion method using the photoelectric conversion device provided with the optical semiconductor electrode of drawing 1.

[Drawing 3] Drawing 3 is an ultraviolet and visible absorption spectrum of the optical semiconductor electrode of Example 4.

[Drawing 4] Drawing 4 is an ultraviolet and visible absorption spectrum of the optical semiconductor electrode of Example 7.

[Description of Notations]

- 1 Optical semiconductor electrode
- 2 Glass substrate
- 3 The layer of ITO
- 4 Titanium oxide layer
- 5 Photoelectric conversion layer
- 6 Adhesive agent
- 7 Lead

- 8 Glass tube
  - 9 Counterelectrode
  - 10 Reference electrode
  - 11 Electrolytic solution
  - 12 Potentiostat
  - 13 Transparent glass cell
-